UDC 666.363.2.001.2

USE OF THE ANION STRUCTURE COEFFICIENT IN DEVELOPING GLASS CERAMIC MATERIALS

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Translated from Steklo i Keramika, No. 6, pp. 7 – 8, June, 2003.

Anion structure coefficients (ASC) are given for solid solutions synthesized on the basis of stoichiometric compositions with a ratio of $Li_2O : Al_2O_3 : SiO_2$ equal to 1 : 1 : 4 – 1 : 1: 12. A fundamental possibility of selecting the residual vitreous phase and predicting the process of sintering of glass powders by calculating the ASC of the initial compositions and the residual vitreous phase in developing glass ceramic materials with preset properties is demonstrated.

Oxides comprising a glass composition, depending on the energy of a single cation – oxygen bond for respective oxygen coordination numbers of ions, can be arbitrarily divided into glass-forming oxides with bond energy over 334.4 kJ and modifiers with bond energy below 250.8 kJ.

It is interesting to make a comparative estimate of the effect of different oxides introduced into silicate or aluminosilicate melts in equimolar or mass quantities on depolymerization of the anion structure. This can be implemented taking into account the effect of oxides on the coefficient of anion structure (ASC) characterizing the anion structure and viscosity of homogeneous melts [1]:

$$\mathrm{ASC} = \frac{\mathrm{O}}{\mathrm{Si} + 0.75\mathrm{Al}},$$

where ASC is the number of oxygen ions contributing to the melt by all oxides related to the number of ions of the central lattice-forming atom [Si, Al].

Consequently, the number of ions introduced into the melt via one percent (weight) silica and one percent aluminum oxide in a tetrahedral coordination with respect to oxygen and incorporated into the anion structure is determined by the following values:

$$\mathrm{Si}^{\mathrm{IV}}_{\mathrm{SiO_2}} = \frac{1}{\mathrm{mole} \times M_{\mathrm{SiO_2}}} = 1.6650 \times 10^{-2};$$

$$\mathrm{Al}^{\mathrm{IV}}_{\mathrm{Al_2O_3}} = \frac{2 \times 0.75}{\mathrm{mole} \times M_{\mathrm{Al_2O_3}}} = 1.4715 \times 10^{-2};$$

$$\mathrm{O}_{\mathrm{SiO_2}} = \frac{1}{\mathrm{mole} \times M_{\mathrm{SiO_2}}} = 3.33 \times 10^{-2};$$

$$\mathrm{O}_{\mathrm{Al_2O_3}} = \frac{3}{\mathrm{mole} \times M_{\mathrm{Al_2O_3}}} = 2.9429 \times 10^{-2}.$$

Calculation of the ASC for ions integrating a glass composition makes it possible to arrange them in the order of decreasing viscosity of homogeneous silicate and aluminosilicate melts. A comparative estimate of the effect of modifier oxides and intermediate oxides introduced into a homogenous melt in equal mass quantities or with an equal mass replacement of one oxide by another on the viscosity of the melt has given the following values of ASC (10^2): 5.5494 for H_2O, 3.3467 for Li_2O, 2.5031 for TiO_2, 2.4802 for MgO, 1.7832 for CaO, 1.6231 for ZrO_2, 1.6132 for Na_2O, 1.4098 for MnO, 1.3918 for FeO, 0.6986 for Cu_2O, 0.6521 for BaO, 0.4480 for PbO.

The depolymerizing effect of oxides on the anion structure of melts and, accordingly, on viscosity decreases in the same order.

Water and oxides of relatively lightweight elements (lithium, titanium, magnesium) have the highest effect on decreasing the viscosity of silicate and aluminosilicate melts. Oxides of heavy elements (lead, barium, copper, etc.) have a significantly lower effect.

The fractional combination method is traditionally used in designing compositions of glass ceramic materials with prescribed physicochemical properties [2].

Glass ceramics have several phases: they consist of crystalline phases (one or several) and a vitreous phase (called residual glass phase). The content of the crystalline phase de-

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pends on the thermal treatment conditions and can be registered in quantitative x-ray phase analysis.

The crystalline phase of high-silica lithium-aluminosilicate glass-ceramic materials with a ratio of $Li_2O : Al_2O_3 : SiO_2$ equal to 1 : 1 : 4 – 1 : 1 : 12 is represented by a series of solid solutions: β-quartz and β-spodumene. We have determined the ASC of the specified compositions (Table 1), which vary from 2.18 to 2.07 and characterize the high viscosity of the melts, which are hard to clarify in melting. For powder technology this is not essential. High viscosity has no effect on the physicochemical properties of materials but determines the sintering process. Materials of stoichiometric compositions 1 : 1 : 4 – 1 : 1 : 12 have high porosity.

According to the research carried out at the State Institute of Glass (GIS) involving identification of the compositions of solid solutions by quantitative x-ray phase analysis, the silica modulus of the solid solutions is lower than the estimated value [2, 3]. The silica modulus is understood as the ratio of the number of silica moles to the number of Li_2O moles.

The developed solid solution of composition 1 : 1 : 4 produces a crystallized solid solution of composition 1 : 1 : 3.8, the composition 1 : 1 : 6 yields a crystallized solid solution 1 : 1 : 5.2, and the composition 1 : 1 : 8 produces a crystallized solid solution of composition 1 : 1 : 6.8. Quantitative x-ray phase analysis of the solid solutions identified the content and composition of the residual vitreous phase [2, 3]. The residual glass phase constitutes high-viscosity quartz glass. The ASC of the residual vitreous phase is equal to 2. The high porosity of the materials of the considered stoichiometric compositions is due to the impossibility for the highly viscous residual vitreous phase to fill the pores of solid solutions formed as a consequence of sintering.

As the composition of the vitreous phase in solid solutions is the same and its quantity varies but little upon variations of the initial composition, the physicochemical properties of materials synthesized depend on their compositions.

To decrease the porosity of such materials and, consequently, to raise their mechanical strength, a vitreous phase is additionally introduced into the composition developed: the mass content of the vitreous phase in glass technology reaches 40 – 60% and in powder technology it reaches 5 – 20%.

Selection of respective compositions for residual vitreous phases makes it possible to control the porosity and to obtain glass ceramics with preset physicochemical properties, including materials with stable TCLE values.

TABLE 1

ASC	Ratio $Li_2O : Al_2O_3 : SiO_2$, %				
	1 : 1 : 4	1 : 1 : 6	1 : 1 : 8	1 : 1 : 10	1 : 1 : 12
SiO_2	64.50	73.20	78.50	82.00	84.60
Al_2O_3	27.40	20.70	16.70	13.90	11.90
Li_2O	8.10	6.10	4.90	4.10	3.50
Initial composition*	2.18	2.13	2.11	2.09	2.07
Composition with lithium aluminosilicate with vitreous phase	2.20	2.15	2.13	2.11	2.16
Residual vitreous phase**	2.18	2.15	2.13	2.12	2.08

* ASC of vitreous phase designed (glass No. 15) is 2.27.

** ASC of residual vitreous phase with lithium aluminosilicate is 2.00.

If glass No. 15 (barium-aluminosilicate glass) is introduced as the vitreous phase, the ASC of the residual vitreous phase of the glass ceramic material will vary from 2.18 to 2.08.

The composition of the glass ceramic material with the fractional composition of solid solution equal to 1 : 1 : 8 and vitreous phase No. 15 is characterized by the same ASC value as the residual vitreous phase, namely, 2.13. This is the reason for the stable TCLE of the glass ceramic material in a wide temperature range.

Thus, the use of the anion structure coefficient together with x-ray phase analysis data makes it possible to predict the process of sintering of glass ceramics materials in the lithium-aluminosilicate system and their physicochemical properties.

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